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Technical Report No. 10

**OBSERVATION OF A MAGIC NUMBER  
IN THE ION DISTRIBUTION OF  
ETHENE CLUSTERS**

by

M. Todd Coolbaugh, William R. Peifer and James F. Garvey\*

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in  
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**Observation of a Magic Number  
in the Ion Distribution of  
Ethene Clusters**

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**Abstract:** We present in this letter the observation of a magic number of  $n=4$  in the  $(C_2H_4)_n^+$  cluster ion distribution only under experimental conditions of low nozzle temperature or high stagnation pressure. We attribute this result not to any special thermodynamic stability of the neutral or ionic cluster, and speculate that it is due to the formation of a  $C_8H_{16}^+$  molecular ion. We feel that this product cation is formed via a series of exoergic condensation reactions which occur within the parent ethene cluster ion. Also presented in this letter are pressure dependence data which are used to elucidate other competing reactive mechanisms.

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## 1. Introduction

The study of chemical reactivity in gas phase van der Waals clusters has become an increasingly active research area. Much of this interest has been generated by the unique position which clusters hold as an aggregate state of matter intermediate between the gas and condensed phases. In addition to this property, clusters provide the physical chemist with the ability to directly observe the effects of stepwise solvation on the course of a simple binary gas phase reaction. An understanding of the effects of solvation is critical in any attempt to forge a union between the disparate fields of gas and condensed phase (solution) chemistry. Although a number of investigators, notably P. Kebarle<sup>1</sup>, have investigated cluster chemistry using high pressure mass spectrometry, recent technological advances have spurred the continued growth of the field. Probably the most important development has been the introduction of high capacity pumping techniques which have made the use of supersonic free jet expansions ('cluster beams') practicable.

Since mass spectrometry currently represents the only means of achieving mass-resolved detection of gas phase clusters, ion-molecule reactions, by necessity, represent the bulk of chemical reactions studied within clusters. This does not present a huge disadvantage however, since many of the products of introcluster ion-molecule reactions resemble transition state structures of reactions occurring in condensed phase media. Indeed previous investigations of ion-molecule reactions in clusters containing organic constituents have revealed some very rich chemistry characterized by extensive bond breaking and reformation.<sup>2</sup> Much of the chemistry which has been observed can be understood in terms of the known bimolecular gas phase chemistry, but a number of 'cluster reactions', that is chemical reactions with no bimolecular gas phase analogues, have also been observed.<sup>3</sup>

When neutral clusters are produced in a supersonic expansion, a distribution of cluster sizes is produced. Following ionization (e.g., via electron impact), a distribution of cluster ions are then produced which are detected mass spectroscopically. However, this cluster ion distribution may have very little resemblance to the neutral cluster distribution since ionization nearly always results in an internally excited cluster.<sup>4</sup> Thus, the ionized cluster may dispose of this excess energy via evaporative processes, i.e. loss of one or more monomer units. Since there is no direct relationship between parent and 'daughter' product ion, analysis of the cluster mass spectra becomes exceedingly difficult. This is further complicated in cases where

exothermic ion molecule reactions or unimolecular decompositions can also occur.

Many of the systems which have been studied consist of ions which are capable of hydrogen bonding. In fact, it has been reported that the intensity distributions of hydrogen bonded cluster ions are very often governed by relative thermodynamic stabilities. That is, structures which correspond to complete solvation shells in which the central ion has all of its hydrogen bonding sites occupied by the solvating species are found to be especially prominent in the mass spectra.<sup>5</sup> The occurrence of such anomalies in an otherwise smooth cluster ion distribution has been termed 'magic numbers'.

However, in a system, such as ethene, where hydrogen bonding is not expected to play a significant role, the observation of pronounced magic numbers is certainly not expected since the distribution of neutral clusters is produced by processes which are essentially statistical in nature. As a result, there would seem to be no *a priori* reason to predict that any particular cluster size should be extraordinarily stable. If magic numbers were observed in such a system, it seems logical that the thermodynamic stabilities of the daughter ion cluster or neutral cluster parent would not be the controlling factors. Therefore the observation of a magic number for the ethene cluster ion system (which will be presented in this letter) would instead appear to be governed by the kinetics of some ion-molecule chemistry occurring within the cluster. We hope to show how our new cluster data may be rationalized in terms of results from gas phase kinetic measurements.

## 2. Experiment.

The experimental apparatus has been described in detail previously<sup>6</sup> and only the essential details will be described here. The cluster source is of the Campargue design<sup>7</sup>. The beam is generated by an adiabatic expansion of neat ethene (Linde, 99.9% purity) through either a 250 $\mu\text{m}$  or 50 $\mu\text{m}$  diameter nozzle ( $d_0$ ). The temperature of the nozzle,  $T_0$ , could be regulated by means of a circulating chiller which flowed coolant through an insulating jacket surrounding the nozzle. The temperature was measured by a thermocouple embeded in the nozzle mount.

Following skimming and collimation, the cluster beam enters a chamber containing the mass spectrometer (Extrel C-50) where it is ionized by electron impact, mass filtered, and detected by an off-axis channeltron. The mass filter is typically operated at better than 0.3 amu mass resolution up to 1200 amu. To assure the validity of the mass spectral data, we regularly calibrated the mass scale and sensitivity of the spectrometer using a PC-based data acquisition system (Teknivent Corp.).

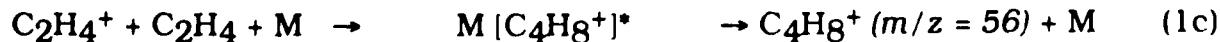
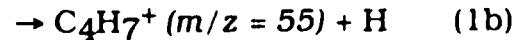
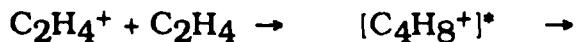
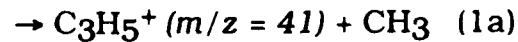
The small (50 $\mu\text{m}$ ) nozzle was utilized to facilitate the measurements of pressure dependence of a number of the smaller ions ( $m \leq 4$ ) found in the cluster mass spectrum (as shown in figure 4). Since the smaller nozzle effectively decreases the clustering efficiency, this has the effect of increasing both the absolute pressures at which any given neutral cluster will be produced as well as increasing the pressure difference between production of neutral clusters (i.e.,  $(\text{C}_2\text{H}_4)_n$  vs.  $(\text{C}_2\text{H}_4)_{n+1}$ ). This is experimentally convenient since it allows the ion products arising from only the dimer to be measured over a substantial pressure interval before products from the trimer begin to interfere, and so on. This technique is very valuable for assigning the first appearance of ions to particular neutral cluster sizes- 'appearance size'. It is possible to infer the opening of reaction channels from larger clusters as a change in slope of the ion intensity,  $I_{m/z}$ , as a function of pressure. This change in slope is quite apparent if the reaction rate of the new channel is appreciably larger than that of the initial channel.

### 3. Results and Discussion.

Figure 1 shows the intensity distributions of the major sequence of cluster ions,  $(C_2H_4)_n^+$ , at several different nozzle temperatures while Figure 2 shows the same intensity distribution as a function of stagnation pressure ( $P_0$ ). The experimental error bars are smaller than the size of the plotted points in Figs. 1-3. In Figures 1 and 2, it can be seen that this ion distribution can be divided into two separate parts. First, ions with  $n < 6$  are found under all operating conditions with much higher intensities than are ions with  $n > 6$ . Secondly, the ions with  $n = 4$  and 5 appear to rapidly grow in as nozzle temperature,  $T_0$ , is lowered or as the stagnation pressure,  $P_0$ , is increased.

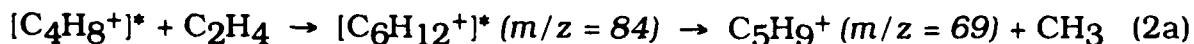
This observation of  $n = 4$  being a magic number under certain expansion conditions is difficult to explain solely in terms of stabilities of either the neutral or ionic parent ethene clusters. While the drop in intensities of the  $n = 2$  and 3 ethene cluster ions may indicate that the population of the parent neutral clusters is being depleted in the production of larger clusters it does not explain why under conditions of extensive clustering the distribution is peaked at  $n=4$  (i.e., why should the  $(C_4H_8)^+(C_2H_4)_2$  cluster ion be so stable?).

In order to fully understand the mass spectra of  $(C_2H_4)_n^+$  system we need to discuss what is currently known concerning the bimolecular ion chemistry between the ethene cation and a neutral ethene molecule. The ion molecule chemistry of ethene,  $C_2H_4$ , has been the subject of numerous experimental and theoretical investigations over the years.<sup>8-15</sup> Much of this interest has stemmed from studies which suggested that the majority of observed ion-molecule reactions of ethene, as shown in reaction (1), proceed through a common intermediate  $[C_4H_8^+]^*$  whose lifetime is long (Field has estimated this lifetime as ca.  $2.9 \times 10^{-7}$  sec)<sup>4</sup>. Support for the mechanism, as

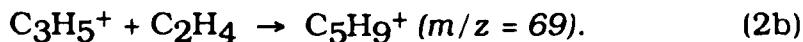


shown in reaction (1), was obtained from high pressure mass spectrometric investigations which revealed that  $C_4H_8^+$  could be efficiently generated via reaction (1c), while reactions (1a) and (1b) were effectively quenched by addition of an inert bath gas.<sup>8,9</sup>

In addition to reaction (1), a series of further condensation reactions could also be observed at higher ion source pressures with the most important of these producing the  $C_5H_9^+$  ion. The question of the mechanism of formation of this ion has generated a certain amount of controversy. Field<sup>4</sup> proposed that this ion arose from alkyl loss from a higher order condensation reaction, reaction (2a),



while Tiernan and Futrell<sup>11</sup> proposed its formation through a sequential reaction via the product of reaction (1a)



Experiments by Kebarle and Haynes,<sup>9</sup> and by Tiernan and Futrell<sup>11</sup> demonstrated that both reactions (2a) and (2b) occur, but that reaction (2b) possesses a much larger rate constant.

Although a number of investigations of the structures of neutral homo- and heterodimers of ethene have appeared, only a handful of investigations of larger ion clusters have appeared. Ceyer *et. al.*<sup>16</sup> investigated the photoionization of ethene clusters and concluded that the ions with empirical formulae  $C_{2m}H_{4m}^+$  and  $C_{2m+1}H_{4m+1}^+$  represented  $C_4H_8^+$  and  $C_3H_5^+$  solvated by ethene's. In two later papers, Ono, *et. al.*,<sup>17</sup> and Tzeng, *et. al.*,<sup>18</sup> arrived at a different conclusion, based on photoionization efficiency and pressure dependence studies, that the ionized ethene trimer rearranges to a  $[C_6H_{12}^+]^*$  intermediate before decomposing. More recently, Buck *et. al.*<sup>17</sup> have presented the results of an experiment in which neutral ethene clusters were size selected by scattering them with a crossed He beam. They concluded that the fragmentation of ethene clusters is dominated by the ion-molecule chemistry of a single  $C_2H_4^+$  ion within the cluster and that the fragmentation patterns are due to the decay of an excited complex  $[(C_2H_4)_n^+]^*$  which must be stabilized by evaporation of  $C_2H_4$  units.

The results which we will now present are consistent with the view that following the initial ionization of the neutral ethene cluster a very rapid

reaction produces excited  $[C_4H_8^+]^*$ . However, we will also make the new speculation that in large clusters, the  $C_4H_8^+$  cation may sequentially react further with other  $C_2H_4$  neutral cluster molecules, with the final products being determined by the kinetics of the various available reaction channels (fragmentation, polymerization, and stabilization) and the overall cluster size.

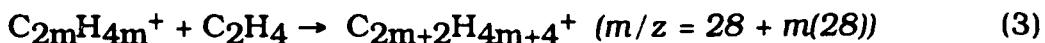
Through a series of experiments, we have observed that at high stagnation pressures,  $P_0$ , or low nozzle temperatures,  $T_0$ , the intensity distribution for the  $(C_2H_4)_n^+$  series of ions is characterized by a strong maximum at  $n = 4$  and an extremely sharp drop between  $n = 5$  and 6. These are just the experimental conditions which should facilitate the growth of very large clusters ( $n \gg 5$ ) independent of the chemical nature of the monomer. From our current observation of anomalous  $(C_2H_4)_n^+$  ion distribution we now feel that the ethene cluster ion mass spectrum is dominated by a series of molecular ions which can be assigned the general empirical formula  $C_{2m}H_{4m}^+$ .

In addition to the pressure/temperature behavior, we have also investigated the effects of electron impact energy on ion production and have measured the pressure dependence of the ion yields for a number of the smaller ethene cluster ions. These measurements have proven especially useful in the analysis of previous static pressure experiments, since they allow us to assign the first appearance of a particular ion species to a given parent cluster size. In some cases, the pressure behavior has been found to be consistent with multiple reaction channels assignable to different size clusters and is consistent with the results of gas phase kinetics studies. However, it is interesting to note that our cluster data bear a strong resemblance to the high pressure mass spectral work of Kebarle and Haynes<sup>9</sup>. This resemblance is especially marked in the strong signals observed for  $n = 4$  ( $C_8H_{16}^+$ ) and  $n = 5$  ( $C_{10}H_{20}^+$ ) as well as the drop off in intensity at about  $n = 6$ . In their paper, Kebarle and Haynes attributed the ions to the formation of  $C_{2m}H_{4m}^+$  cations via condensation reactions.

Based on this comparison with existing high pressure work<sup>9</sup>, we speculate that the cluster ions we observe between  $n = 2$  and 6, also represent the products of a series of intracluster condensation reactions. That is, the observation of the magic number at  $n = 4$  (under expansion conditions which create extensive clustering) is due to the formation of the  $C_8H_{16}^+$  molecular ion which is generated via a series of intramolecular ion-molecule reactions within the cluster.

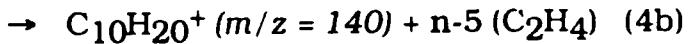
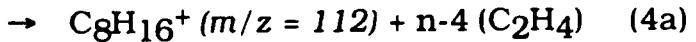
If this interpretation is correct, the rates of these internal condensation reactions certainly must fall off very dramatically after the addition of three or four ethene monomers to the ethene ion. Kebarle and Haynes estimated rate

constants for successive condensation reactions of the form



and noted that the reaction rates decreased rapidly as the size of the product ion increased ( $k_m$  :  $k_1 = 10^{-9}$ ,  $k_2 = 2 \times 10^{-12}$ ,  $k_3 = 8 \times 10^{-13}$ ,  $k_4 = 2 \times 10^{-13}$ ,  $k_5 = 8 \times 10^{-14} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}$ ). This decrease in rate constant as a function of increasing  $m$  was attributed to steric effects. That is, since the charge will preferentially seek a tertiary or quaternary position, the larger  $C_{2m}H_{4m}^+$  ions should be highly branched and as a result progressively less reactive.<sup>9</sup>

As seen above with gas phase bimolecular rate constants<sup>9</sup>, we might then also expect a drop in the cluster reaction rate as the size of the cluster increases. This is again due to the highly branched  $C_{2m}H_{4m}^+$  product cations being less reactive. In addition, since these condensation reactions are exothermic<sup>20</sup>, we would also expect extensive evaporation of unreacted monomers from the cluster. In summary, large neutral  $(C_2H_4)_n$  clusters, following ionization via electron impact, can react within the cluster to give primarily bare  $C_8H_{16}^+$  and  $C_{10}H_{20}^+$  product cation, as shown in reaction (4). The intensity of these



ions would then be expected to increase as the distribution of the neutral ethene clusters grows larger (i.e., as either  $T_0 \downarrow$  or  $P_0 \uparrow : n \uparrow$ ). As a result, we speculate that this prominent peak at  $n = 4$  represents a balance between two competing effects. We expect that the larger the cluster, the greater the probability of reacting internally via reaction (3), due mainly to the increase in the number of  $C_2H_4$  molecules. However, as the cluster size increases the rate constant also decreases<sup>9</sup> (apparently due to steric effects). This is a brand new interpretation on the nature of these ethene cluster mass spectra, in that they are attributed to a single molecular ion and not a cation solvated by neutral monomers.

Figure 3 shows the variation of the relative intensities of these ions as a function of electron energy. This figure shows that at high electron energy, the

relative intensities of the  $n = 2$  and 3 ions increase while the intensities of ions with  $n > 4$  decrease. Indeed we also observed that the relative intensities of other small product ions at  $m/z = 41, 69$ , and 97 also increased with increasing electron energy. Other previous investigations have shown that the outcome of the ethene ion molecule reaction is dependent on the ion internal energy.<sup>10,13</sup> The variation of the ion intensities with electron energies presented in figure 3 may also be rationalized on the grounds that as the ion energy increases, intermediates become more energetic and the evaporative processes may not be as efficient in stabilizing the intermediate ion. It might also be expected that this less efficient stabilization may lead to the production of more  $C_4H_8^+$  ions with sufficient excess energy to decompose into  $C_3H_5^+$  ions hence the increased prominence of the ions at  $m/z = 41, 69$ , and 97.

In addition to these condensation reactions, a number of other competing reactions may also take place. These include fragmentations and decompositions (alkyl loss from excited intermediates). Taking into account the possibility that the decomposition products may also undergo condensation and stabilization reactions, the final cluster distributions will depend on the kinetics of the possible reactions which a given cluster may undergo and on the distribution of the neutral parent clusters. Figure 4 shows the results of a pressure dependence study using a 50  $\mu m$  nozzle and low electron energy (13 eV). The panels show, from top to bottom, ion products which we have assigned as arising from the neutral dimer, trimer and tetramer (reaction scheme 1). At the lower pressures ( $3 \text{ atm} \leq P_0 \leq 5 \text{ atm}$ ) the  $m/z = 41$  and 55 ( $C_3H_5^+$  and  $C_4H_7^+$  respectively) are the only ions observed larger than the monomer. Between  $5 \text{ atm} \leq P_0 \leq 7 \text{ atm}$  products from the neutral trimer (middle panel) begin to appear. The ion at  $m/z = 56$  ( $C_4H_8^+$ ) is by far the most abundant of these and most likely results from evaporative loss of an ethene from the trimer. The ions at  $m/z = 42$  and 43 are minor products and are believed to represent decomposition of a  $[C_6H_{12}^+]^*$  intermediate. The bottom panel shows that for  $P_0 \geq 7 \text{ atm}$  products arising from ionization of the tetramer begin to appear at  $m/z = 69$  and 84 ( $C_5H_9^+$  and  $C_6H_{12}^+$  respectively). The  $C_6H_{12}^+$  arises from evaporative stabilization of the tetramer while the  $C_5H_9^+$  arises from methyl loss from the  $[C_6H_{12}^+]^*$ .

One last observation concerning the alkyl decomposition channel may be of considerable interest. We observe that the intensity of a series of cluster ions, which can be assigned the general empirical formula  $C_{2m+1}H_{4m+1}^+$ , falls off rapidly with increasing  $m$ . It would appear then that the alkyl loss reaction is efficiently quenched in clusters containing greater than five ethene

molecules. It may be that the alkyl loss mechanism requires a skeletal rearrangement which is blocked in some way by extensive solvation. Work is currently underway to more fully understand this effect.

### **Acknowledgments**

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7) For  $m = 1$ , reaction (3) has a  $\Delta H^0 = -(32-60)$  kcal/mole<sup>21</sup> depending on the structure of the product.

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**Figure Captions**

Figure 1)  $(C_2H_4)_n^+$  ion intensity distribution as a function of nozzle temperature ( $T_0$ ):  $P_0 = 1.5$  atm.,  $d_0 = 250\mu m$ , electron energy = 70 eV.

Figure 2)  $(C_2H_4)_n^+$  ion intensity distribution as a function stagnation pressure ( $P_0$ ):  $T_0 = 297K$ ,  $d_0 = 250\mu m$ , electron energy = 13 eV.

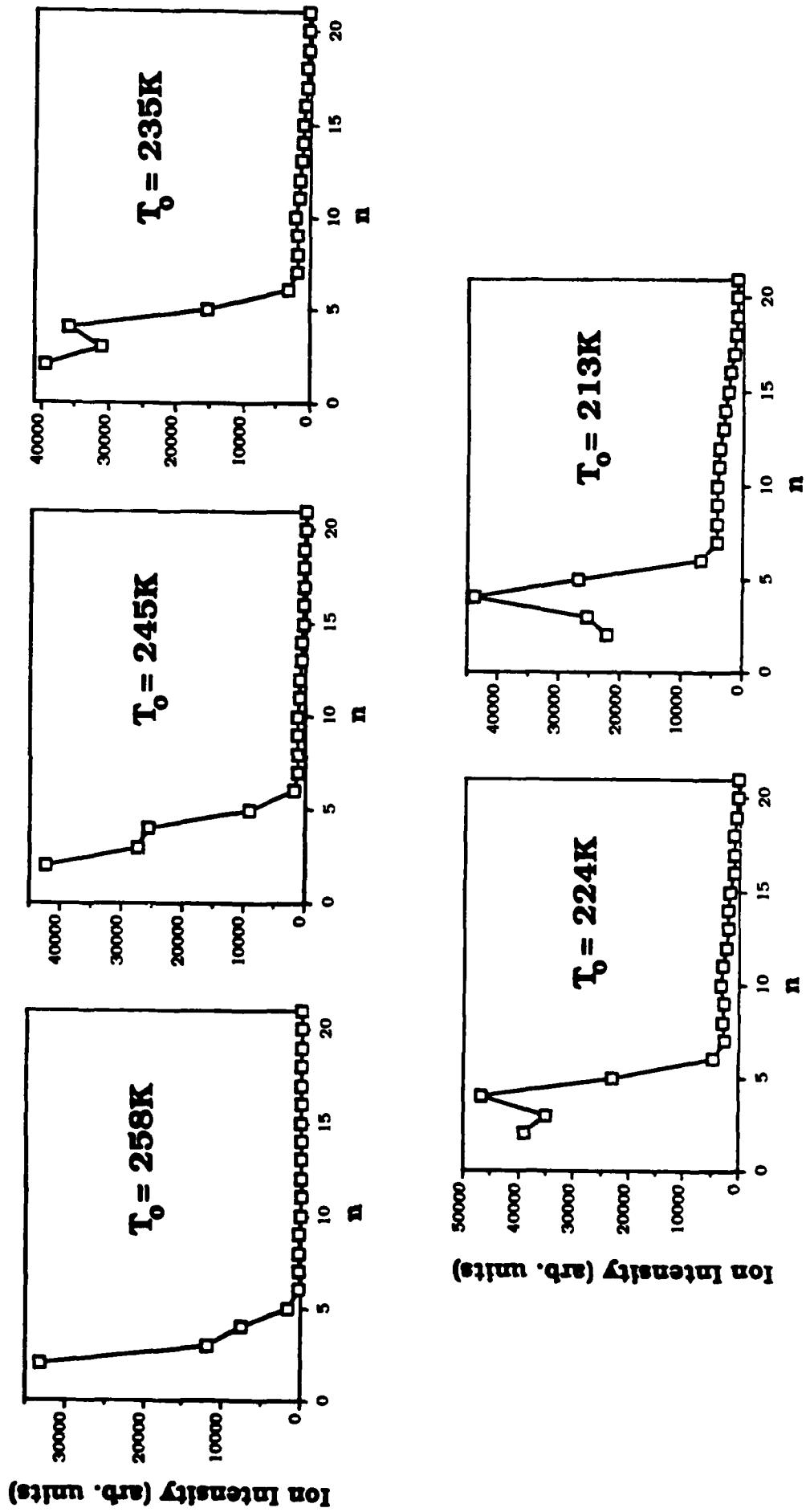
Figure 3)  $(C_2H_4)_n^+$  ion intensity distribution as a function of electron energy:  $P_0 = 4.0$  atm.,  $T_0 = 296K$ ,  $d_0 = 250\mu m$ .

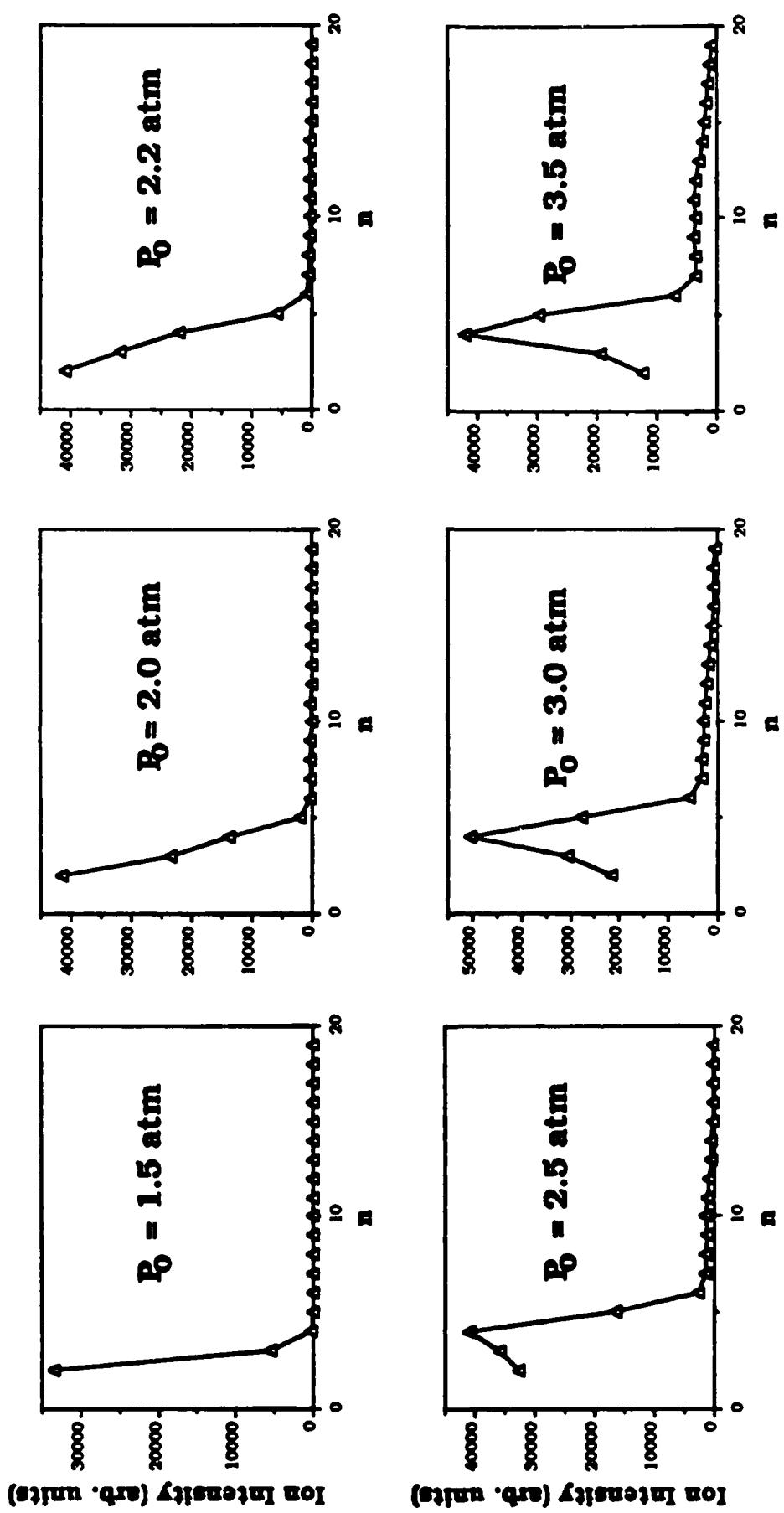
Figure 4) Normalized intensities of product ions produced via electron impact of  $(C_2H_4)_n$ , as a function of source pressure ( $P_0$ ).  $T_0 = 250K$ , electron energy = 12.8 eV,  $d_0 = 50\mu m$  Error bars represent a standard deviation. In order to distinguish common parent cluster ions, we have deliberately grouped product ions with similar pressure dependences. Reaction Scheme 1 indicates the smallest possible parent ion cluster which can generate the observed product ion

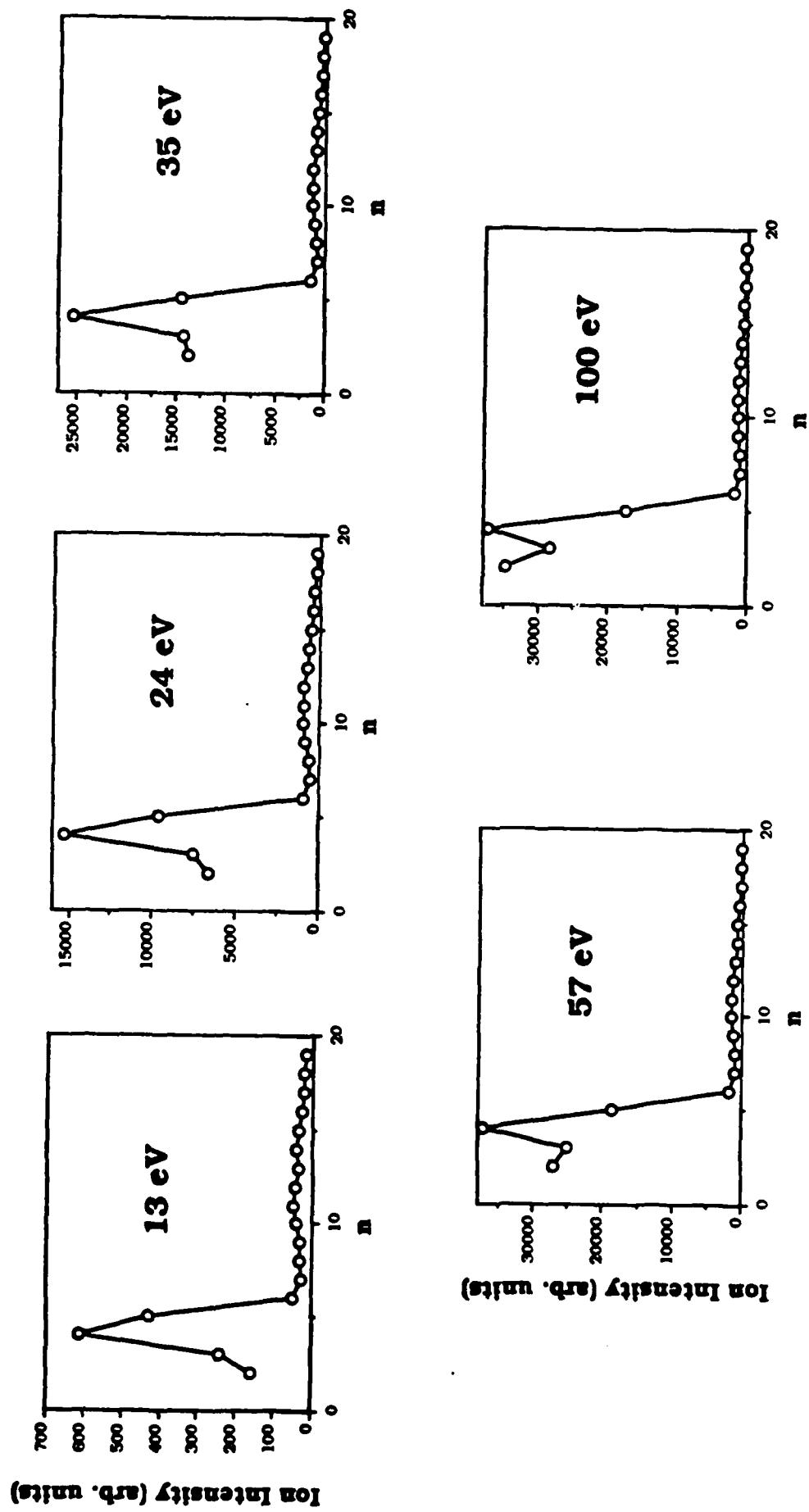
Top panel)  $C_3H_5^+$  and  $C_4H_7^+$  which appear at 1.5 atm

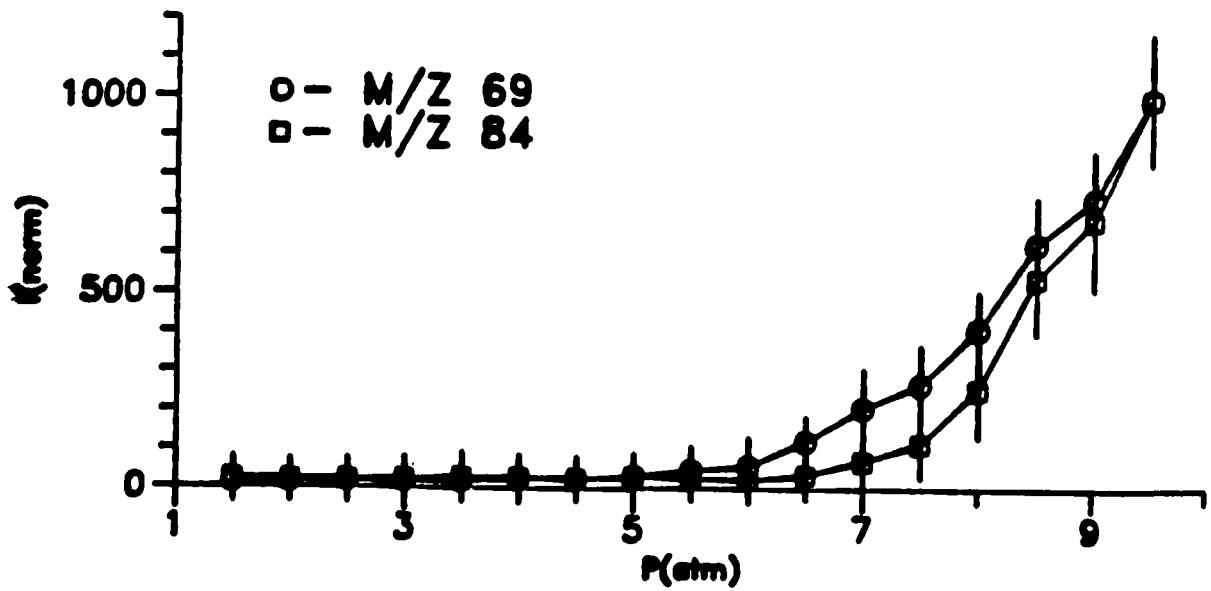
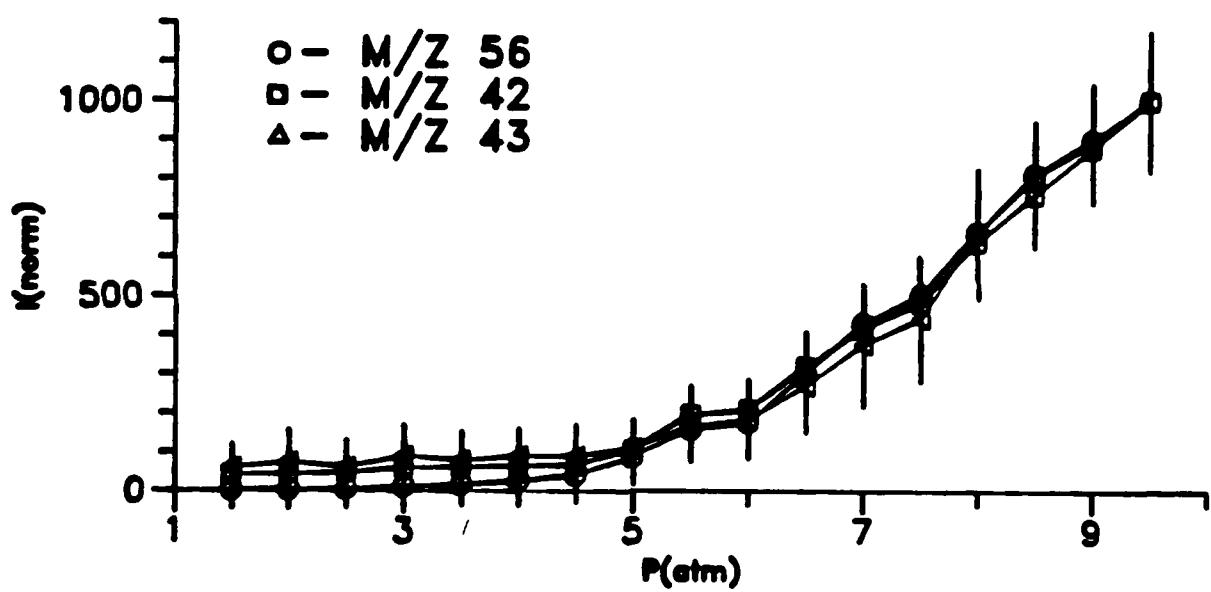
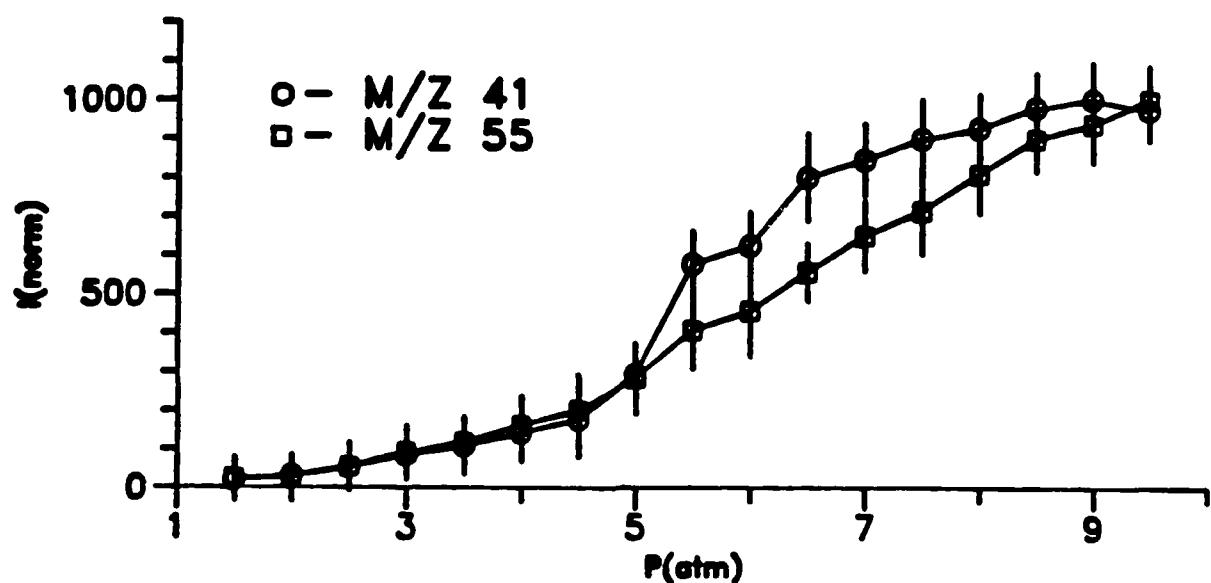
Middle panel)  $C_4H_8^+$  as well as  $C_3H_7^+$  and  $C_3H_6^+$  which appear at 4.0 atm

Bottom panel)  $C_6H_{12}^+$  and  $C_5H_9^+$  which appear at 6 atm.

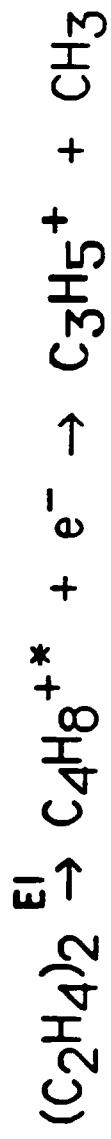








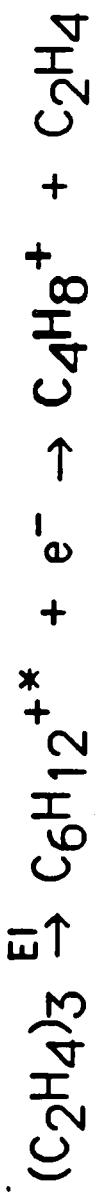
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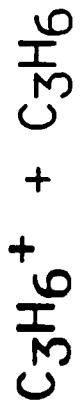
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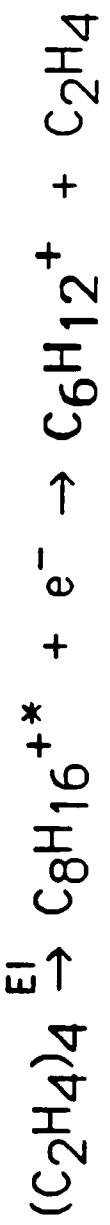
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84



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Reaction Scheme I